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Research on Natural Superhydrophobic Surfaces and Synthetic Superhydrophobic Surfaces

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Abstract

In recent years, superhydrophobic coatings have unique properties such as water repellency, anti-fog, anti-icing, and can realize surface self-cleaning, fluid drag reduction as well as oil-water separation. The microscopic-graded-rough structure of the energy substance and the surface determines the hydrophobicity of the surfaces. This article describes the principles of superhydrophobic surfaces such as Yong's angle, and lists some natural superhydrophobic surfaces including Lotus Leaves, Rose petals, Butterfly wings and rice leaves. At the same time, this article also describes how to prepare synthetic superhydrophobic surfaces, like roughening and coating to created one-level hydrophobic structure and how to manufacture two-level structures, and explains the advantages and disadvantages of these methods. Finally, we introduced some methods for evaluating superhydrophobic surfaces.

Keywords

Superhydrophobic surfaces, Yong's angle, Coating; Roughening, Evaluation of structure.

1. Introduction

1.1 Definitions

For a liquid or solid, the layer of molecules or atoms that forms its surface is said to experience surface tension or possess surface energy. Surface tension or surface energy is the result of particles on the surface experiencing different cohesion forces compared to particles inside the liquid or solid. This is because particles on the surface are not fully surrounded by like particles and thus cohere strongly to those next to them in the surface layer in order to minimize the surface area. Liquids and solids have the tendency to minimize their surface area due to the need to keep their particles together in a fixed volume. Thus, particles on the outside need to sustain a tension force similar to what a stretched membrane experiences and have a higher potential energy than those inside the substance do.

To define surface tension, consider a liquid film spread over a rectangular frame, which has a mobile slider that can change the surface area of the liquid film. The film is thick enough (1μm) to prevent overlapping of the two inter- facial regions. If we increase the surface area by moving the slider a distance dx, work is done on the liquid film. The work done dW is proportional to the increase in

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surface area dA by a proportionality constant γ . The constant γ is called surface tension [7]. The surface tension γ has a unit of J/m² or N/m.

When a solid is in contact with liquid, the molecular attraction will reduce the energy of the system below that for the two separated surfaces. This is shown by the Dupré equation

$$W_{SL} = \gamma_{SA} + \gamma_{LA} - \gamma_{SL}$$

Where $W_{SL}$is the work of adhesion between the solid and liquid per unit area, γ_{SA} and γ_{SL} are the surface energies of the solid against air and liquid, and γ_{LA} is the surface energy of liquid against air [5].

As a result of surface tension of liquids and solids, a liquid droplet will come into contact with a solid surface at a certain angle called the equilibrium contact angle . The contact angle can be obtained by the Young's equation

$$cos\theta = \frac{\gamma_{SA} - \gamma_{SL}}{\gamma_{LA}}$$

In the case of water droplets on a solid surface, the magnitude of the contact angle determines hydrophobicity or hydrophilicity of the solid surface. When $\theta \approx 0^o$, the surface is said to be superhydrophilic; when $0^o < \theta < 90^o$, the surface is hydrophilic; when $\theta > 90^o$, the surface is hydrophobic; when $\theta > 150^o$, the surface is superhydrophobic [32].

While the wettability of surfaces depends on the magnitude of contact angle, surfaces' ability to repel water is affected by the extent of contact angle hysteresis. Contact angle hysteresis is a difference between the advancing and receding angles. It arises from surface roughness, porosity and chemical hetero- geneity and is an indication of how easily liquid droplets can roll off a surface [9]. Consider a liquid droplet in contact with a tilted surface. If there is no contact angle hysteresis, the droplet will start sliding off the surface immediately upon contact due to gravity. However, if the contact angle hysteresis is significant, the droplet may stay on the surface even when the surface is vertical. Hence, in real-life applications, a desirable superhydrophobic and self-cleaning surface would exhibit both a large contact angle and low contact angle hysteresis.

1.2 Natural Superhydrophobic Surfaces

Researchers have found that many plants and insects have surfaces that ex- hibit superhydrophobic properties, with the most common examples including lotus leaves, rose petals, butterfly wings and rice leaves. These surfaces display contact angles higher than 150° with water, while the contact angle hysteresis may be high or low for different surfaces, leading to varying wetting properties. In this review, we are going to examine the similarities and differences among wetting properties of different natural superhydrophobic surfaces and account for these traits. This in turn will form the basis for our discussion about the synthesis of synthetic superhydrophobic surfaces.

1.3 Synthetic Superhydrophobic Surfaces

Artificial superhydrophobic surfaces can be fabricated by two methods: Man- ufacture rough surfaces that are subsequently coated with a low-surface energy material or use low surface energy materials that are subsequently roughened. Superhydrophobic materials are extensively used based on their properties of self-cleaning, waterproofing, drag reduction. This surface material can be used in the domain of oil-water separation, rain-proof equipment, targeted drugs as well as many other applications. Nowadays, the synthetic superhydrophobic surface materials are mainly silicon based materials or fluorine-containing mate- rials. Compared with silicon materials, fluorine-containing materials have been widely applied because of lower surface energy and superior resistance to heat and chemicals. The subsistent artificial superhydrophobic surface technology is immature and it is worthwhile devoting much effort to this. Based on the existing technology, complex production processes and undesirable long term durability of the superhydrophobic surface material is less successful and still requires further research before putting into the field or a range of different industrial applications.

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1.4 Scope of Article

This report basically introduces several insects and plants with superhy- drophobic characteristics and analyzes how surface structure and chemical com- position affects the hydrophobicity of the surface. Based on the study of the common characteristics of different superhydrophobic organisms, this report in- troduces several common methods of superhydrophobic surface manufacturing, such as photo lithography, precipitation and casting, and analyzes their advan- tages and deficiencies. Research shows that artificial superhydrophobic surfaces usually do not have long-term durability. Therefore, the feasibility and ma- jor challenges of making a durable artificial superhydrophobic surface are also discussed in this report.

2. Factors that Determine Superhydrophobicity

2.1 Introduction of Wetting Systems

2.1.1 The Wenzel State

The Young's equation determines the equilibrium contact angle of liquid on smooth surfaces, while the contact angle of liquid with a rough surface is characterized by the Wenzel and Cassie–Baxter equations.

First, consider a liquid droplet on a rough surface with a homogeneous interface. The contact angle of the liquid droplet upon the rough solid surface θ is related to the contact angle θo upon a smooth surface, through the Wenzel equation

$$cos\theta = R_f cos\theta_o$$

Where Rf is the roughness factor of the solid surface, given by the ratio of its rough surface area ASL to its flat projected area AF , i.e.

$$R_f = \frac{A_{SL}}{A_F}.$$

In the Wenzel state, both wetting and non-wetting properties of solid surfaces are enhanced by roughness. Consider a hydrophobic rough surface. When $\theta > 90^o$, $cos\theta < 0$, $cos\theta_o$ becomes more negative as $Rf > 1$, making θ_o even larger. This means the hydrophobicity of a solid surface will be reinforced by its surface roughness. On the other hand, for a hydrophilic rough surface, $\theta < 90^o$ and $cos\theta > 0$, roughness makes $cos\theta_o$ more positive, leading to smaller θ_0. Hence, a hydrophilic solid surface will also become more hydrophilic.

2.1.2 The Cassie-Baxter State

Consider a liquid droplet on a rough surface with a heterogeneous interface, i.e. both solid-liquid and liquid-air interfaces are present. The two fractions of the heterogeneous interface have fractional areas f_1 and f_2 and local contact angles θ_1 and θ_2 respectively, where $f_1 + f_2 = 1$. The apparent contact angle θ is given by the Cassie equation

$$cos\theta = f_1 cos\theta_1 + f_2 cos\theta_2$$

When there are air pockets between the liquid and the rough solid surface, the composite interface consists of a fractional geometrical area of the solid- liquid interface under the droplet and the liquid-air interface. Let $f_1 = f_{SL}$, $\theta_1 = \theta$, and $f_2 = f_{LA} = 1 - f_1$. Since the contact angle is 180o for air, θ2 = 180^o and $cos\theta_2 =1$. In this case, the apparent contact angle $\theta*$ is given by the Cassie-Baxter equatio

$$cos\theta^* = R_f f_{SL} cos\theta + f_{LA} cos\theta_2$$

$$cos\theta^* = R_f f_{SL} cos\theta \text{-} f_{LA}$$

$$cos\theta^* = R_f f_{SL} cos\theta + f_{SL} \text{-} 1$$

2.2 Hierarchical Structure

Based on scientists' research on organisms with superhydrophobic surfaces, it is found that some superhydrophobic organisms have distinct hierarchical structure on their surfaces. Frequently, hierarchical structures are realized by the combination of multi-level micron structure and

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nanostructure self-assembly [20](Figure 1). When a surface has a smaller nanosecond structure on the papillae which constitute the roughness of the surface, this surface has a hierarchical structure. At present, a large number of research results have shown that the hydrophobicity of some biological surface is caused its micro-nano structure characteristics. In addition, the micron and nanometer combined hierarchical structure also plays a role in determining the surface infiltration of biological surface [3]. Compared with other surface materials, the surfaces with hierarchi- cal structures have better hydrophobicity.

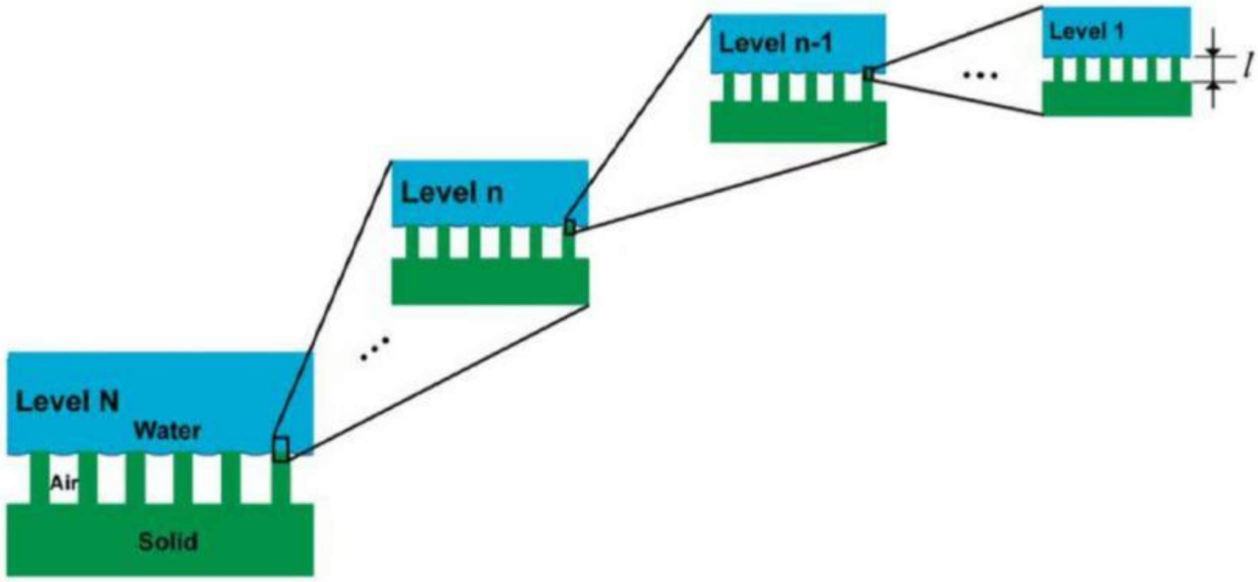

Figure 1. The several hierarchical structures on the surfaces [42]

By analyzing Cassie-Baxter state and generalizing it to higher levels of the hierarchical structure, the recurrence relation can be find as,

$$\theta_n = arccos(f_n cos\theta_{n\text{-}1} + f_n\text{-}1)$$

Where, the subscript n denotes the level of the surface structure. By substituting the expression for n-1 into the equation for n, the explicit expression of the apparent contact angle of the Nth level as

$$\theta_N = \arccos\left(\prod_{n=1}^{N} f_n \cos\theta_0 + \prod_{n=1}^{N} f_n - 1\right)$$

According to the research, the smaller the minimum hierarchical structure is within limits, the better the hydrophobicity of the surface is. In addition, the hydrophobicity of hierarchical structure is also related to pressure. Under the action of pressure, the minimum hierarchical structure is that the liquid contact will appear Wenzel state, and the surface hydrophobicity will also be reduced.

2.3 Role of Surface Structure and Chemical Composition

It is discovered that surface structure and chemical composition are two key factors affecting the hydrophobicity of surface materials. Generally, low surface free energy of the material as well as surface roughness is able to imbue hydrophobicity. Surface energy comes from the uneven distribution of molecules or atoms around the surface, resulting in uneven interaction between the sur- face molecules, so that a force perpendicular to the surface and inward is generated. (van der Waals forces). As a result, highly electronegative elements are more suitable for the manufacture of superhydrophobic surfaces, because highly atoms with highly electronegative are more likely to form stable structures of the outermost eight electrons, which are less likely to generate van der Waals forces with other groups. In addition, material with low surface energy has poor absorption. This kind of material shows low water absorption. Increasing the surface roughness also can improve the material's hydrophobic capacity. It can be illustrated as: Electro negativity determines the hydrophobicity of materials.

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3. Natural Superhydrophobic Surfaces and Characterization

3.1 Lotus Leaves

3.2 Introduction

The lotus leaf is famous for its self-cleaning ability. The main cause of this effect is the special structure of its leaf surface. There are papillae on the leaf surface known as microstructure while the waxed texture upon it is referred to as the nanostructure [33].The microstructure can only increase high contact angle, but it is the combination of the microstructure and the nanostructure that provides the lotus leaves with high hydrophobicity(low hysteresis with high contact angle and low sliding angle (Figure 2)[11]. Because of the hydrophobic surface, the droplet receive little resistance when rolling on the surface. The droplet is able to pick up the fouling materials through its way because the adhesive force of the surface is too small compared with the adhesive force of the droplet due to its strong surface tension [17].

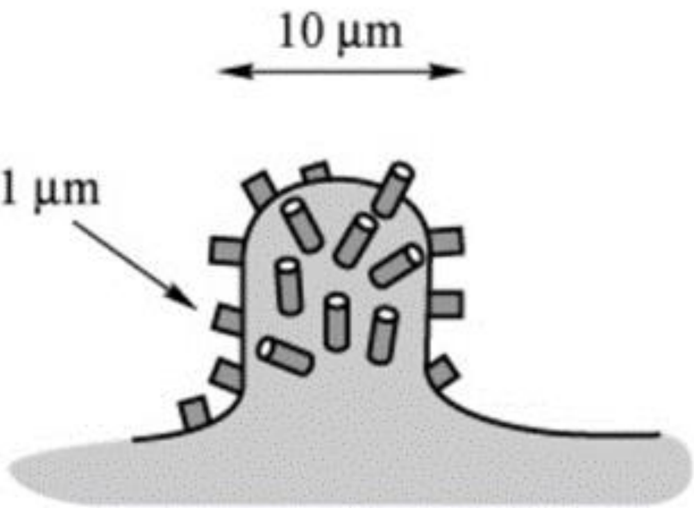

Figure 2 A simple image describing the hierarchical structure

3.2.1 layer

On the epidermal cells of the lotus covers a micro surface mainly made up of waxen crystal excreted from the cells. The wax layer on both front and back side of the leaf can be either observed without any assistant devices or recognized by touching it directly. The purpose of this chapter is to find out the properties of such wax layer and what part it plays in making lotus leaf a hydrophobic surface.

3.2.2 Removal of Wax Layer

Another feature of the hydrophobic lotus leaf is the papillae structures on the surface. After the wax layer is removed, superhydrophobic surface's contact angles decrease dramatically, while the contact angles hydrophobic surface have little changes through the same process [4]. This is because the wax layer plays an important part in reducing the contact area as well as making the contact angle bigger. It also provides roughness so that the liquid cannot enter the surface easily. When the micro structure of the wax crystal disappears, the air inside the plastron kept between the liquid and the solid is very likely to flee since there is no more layers preventing it from leaving. In this way, the state of the leaf transfers from Cassie state to Wenzel state [17].

3.2.3 Optical Proftler

The papillae on the leaf surface are another reason of hydrophobicity. These papillae increase the contact area(which is referred to R^f in the Cassie state) and create air pockets. It can be easily inferred that the factors of these papillae will have a direct influence on the hydrophobicity (Figure 3). The first factor that is going to be mentioned is height.

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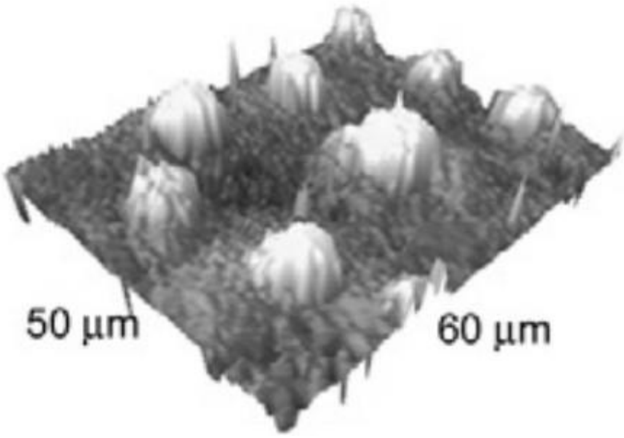

Figure 3. Papillae observed through optical profiler Bharat Bhushan and Yong Chae Jung. [5]

In accordance with the graphs illustrating the height of the papillae obtained through optical profiler, we can have a clear characterization of the structure. It will also help us figure out the relation between height and the contact angle. It can be inferred that as the papillae's height decreases, the chances of creating air pockets decrease as well, which results in the relatively weaker effect on the contact angle [5].

3.2.4 AFM Observation

Characterization provided by AFM allows us to obtain different parameters such as the distance between the papillae and also the height and radius of them.

Adhesive force:

The adhesive force can be affected by several factors, one of which is dry- ness. Dried leaves of lotus have lower adhesive force than the fresh ones. This is because the fresh one have moisture inside there leaf structure, which enables them to deform when the surface contact with liquid [4]. As the surface deform, larger contact area is created, and the adhesive force increases. When the leaves are dried, there won't be any moisture left in the structure, and the adhesive force decreases.

Friction & Hierarchical:

The same as the adhesive force, the friction is also affected by the practical contact areas. This also explains why the friction effect decreases as the scale of scanning decreases from nanostructure to microstructure since the distance between papillae are far much bigger, which decreases the possibility for plas- tron to form. Compared with microstructure, the nanostructure surface has a relatively high roughness. As the scale increases, contact angle and contact hysteresis increases [5]

3.3 Rose Petals

3.3.1 Introduction

Different from the lotus leaf, though rose petals present similar hydrophobic- ity, it can also make the droplet which is supposed to slide down due the garvity cling tightly to its surface. The explanation of such effect is considered to result from the combination of micro and nanostructure (Figure 4).

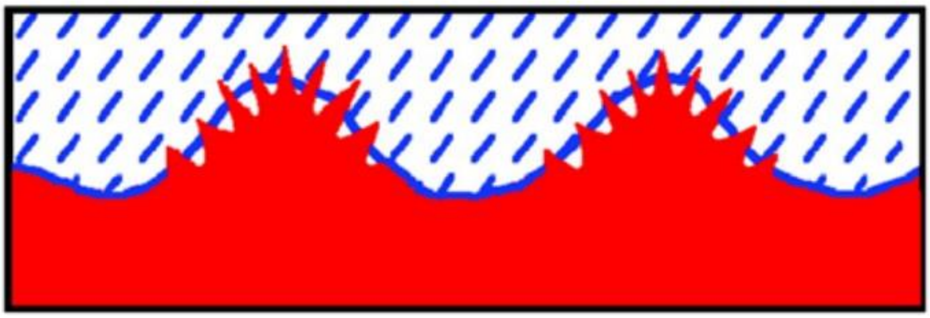

Figure 4. The rose petal surface structure rebelling against water [43]

3.3.2 Surface Structure

When the droplet has contact with the surface, the contact area is reduced due to the micro papillae structure, which makes the surface hydrophobic. However, the papillae of rose petals are not as tall the lotus's, also, the distance between rose papillae is relatively longer than lotus papillae (Figure 5). If the droplet advance further into the surface, the air pockets between the liquid and solid created by the papillae are filled by water, which means the contact area between the liquid and air no longer exist, making the state convert from Cassie to Wenzel [10].As the contact area becomes larger, contact angle hysteresis is increased as well as the surface tension [4].

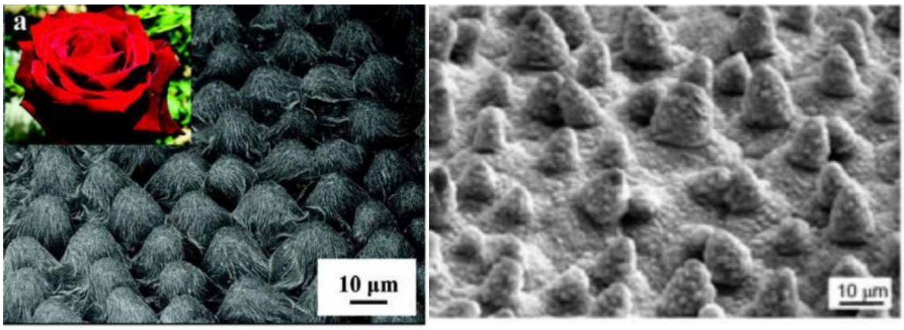

Figure 5. Two images of the comparative structure of the rose petal(upper) and the lotus leaf [4] [43]

3.3.3 Rose Petals with Low and High Adhesion Force

Rose petals are found to be equipped with either low adhesion or high adhesion in different cases. A droplet can still stay on the back side of a petal without rolling down due to the high contact angle which provides high adhesion force, while a droplet will be unable to keep itself on a petal which has only little adhesion force. The reasons lies in whether the petal is dry or wet [4].

3.3.3.1 Surface Deformation

Although the two different types of petal both have hierarchical structure, they differ in spacing distance, the peak-to-base height of their microstructure, and the density of nanostructures (Figure 6). Rose petals with low adhesion are found to have smaller spacing distance but larger height than the ones with high adhesion, which is believed to be the reason of the low adhesion effect resulting from the drying process. The contact angle of the petal decreases when it is dried since the microstructure is found to shrink, causing the decrease in both height and distance, which has an influence on the contact angle. Because the formation chances of air pockets mainly depend on the height and distance, and other physical parameters of structure, it can be inferred that the contact angle will be influenced in consequence [4].

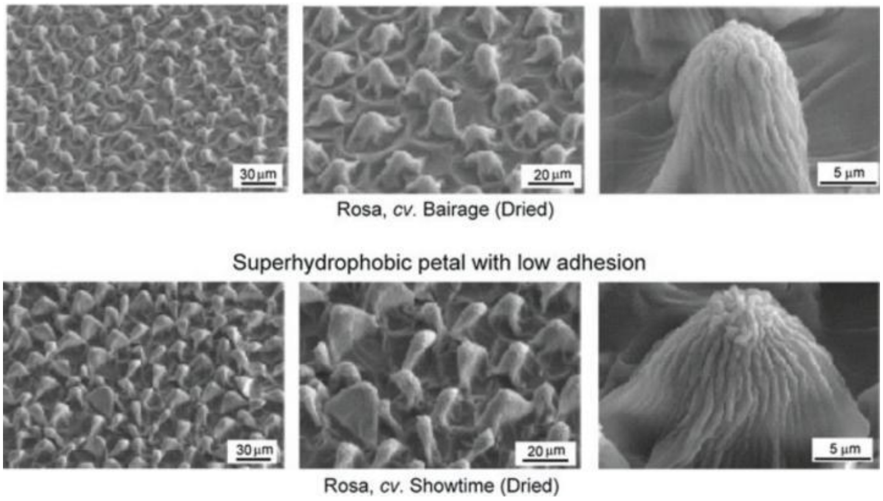

Figure 6. Images describing the difference between the two states [5]

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3.3.3.2 Moisture

The change in adhesion force not only results from the self-change caused by the process, but is also related to other exoteric factors. There exists moisture in the wet leaves and petals of the plant, which can soften the surface and make it to deform itself, creating a larger contact area to increase the adhesive force. Besides enlarging contact spaces, the moisture has another effect, that is to decrease the friction force of the surface, which has similar influence on the droplet as the adhesion force does[4]

3.4 Butterfly Wings

3.4.1 Introduction

The hydrophobicity of the butterfly wings mainly depends on the surface scale and the air pockets that form inside it. The image below reproduced from Bhushan. Biomimetics:bio inspired hierarchical-structured surface. Springer, 2016 describes the structure of the butterfly wings (Figure 7).

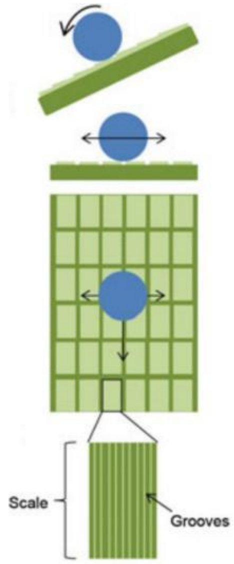

Figure 7. The structure of butterfly wings [4]

3.4.2 Scale(Shark Skin Effect)

When the droplet make it through the wing surface in the radial-outward direction, the terminal part of the scale on the surface turn up, creating enough space for the air to enter. As air pockets are created, the contact surface between the wing surface and the liquid is decreased, which makes it easier for the droplet to slide down the surface. On the opposite, if the droplet goes against the radial-outward direction, it will receive huge adhesion force since the contact area increases [35].

In sum, the scale on the wings provides anisotropic flow, which is quite similar to the riblets structure on shark skins. The effect of both two structures have a great control on drag reduction, and will only be triggered in the right direction [4]. The image below presents the two situation (Figure 8).

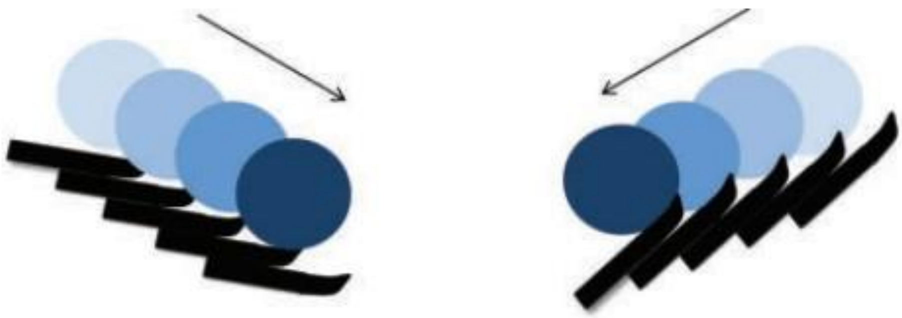

Figure 8. Two situation along radial-outward direction/against radial-outward direction

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3.4.3 Microgroove (Lotus Effect)

The shark skin effect consists of anisotropic flow, superhydrophobicity, and low adhesion. As the scale provides anisotropic flow, the other two effects cer- tainly come from the microgrooves on the scale. The longitudinal microgrooves are found to reduce drag and make the surface hydrophobic [4] (Figure 9).

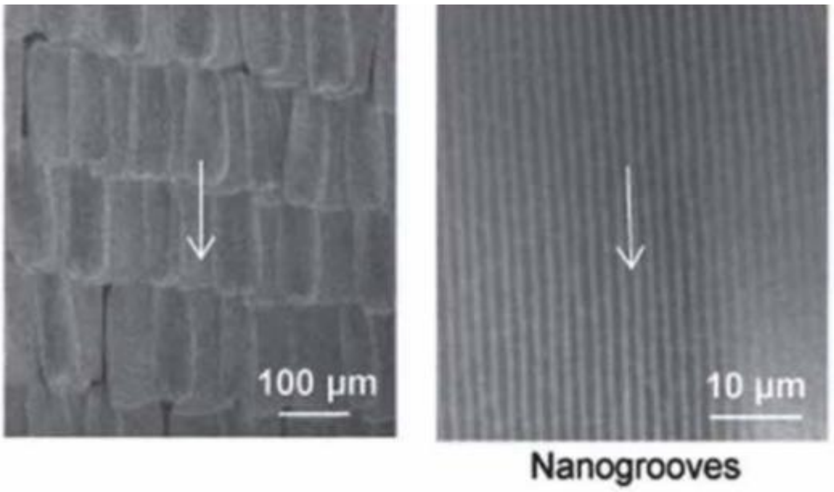

Figure 9. Nanogroove structure [4]

3.5 Rice Leaves

3.5.1 Introduction

The lotus leaf is famous for its hydrophobicity benefit from the papillae struc- ture on its leaf surface. People found that a droplet was able to slide to anywhere on the lotus leaf by overcoming only little drag force, while later, people dis- covered the hydrophobicity of another plant named rice leaves, whose effect on liquid is different from the lotus effect.

The image below reproduced from Bhushan. Biomimetics:bio-inspired hierarchical- structured surface. Springer, 2016 describes the structure of the rice leaves (Figure 10).

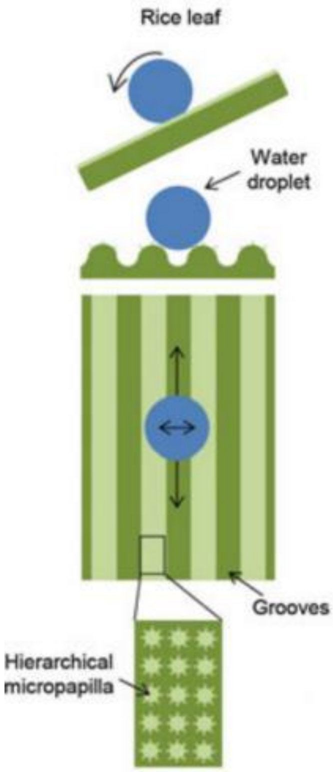

Figure 10. The structure of the rice leaf [4]

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3.5.2 Papillae (Shark Skin Effect)

Though equipped with both micro and nanostructure (referred to as hierarchical structure)just as the lotus does, the rice leaf gives an anisotropic effect on the droplet. The reason lies in the special distribution of the papillae. The papillae arrange in lines neatly along the direction in which the leaf margin reaches out, however, the papillae are not in order on the transverse direction (Figure 11). Because of that, the rolling angle of the droplet also varies on different directions, for example, the longitudinal angle is about $3^{o} - 5^{o}$, while the transverse angle is about $10^{o} - 15^{o}$ [13].

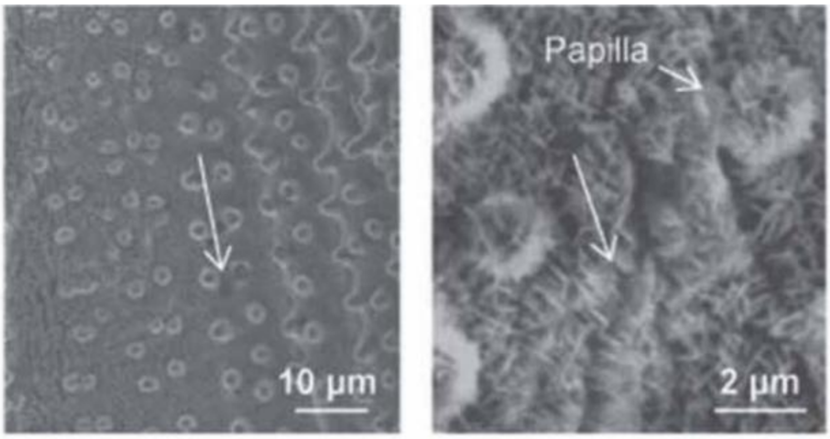

Figure 11. Papilae [4]

3.5.3 Bumps (Lotus Effect)

It is known that rice leaves have hierarchical structure. Besides papillae structure, there are also waxy nanobumps on the micro papillae structure. It has many properties similar to the lotus waxy layer structure[4].The lotus effect superhydrophobicity and low adhesion is facilitated by self-assembled epicuticular waxy nanobumps in rice leaves[4] It now can be confirmed that besides lotus, many other plants also have developed self-cleaning properties due to super- hydrophobic and low adhesion characteristics in various ways such as forming papillae structures[4] .

4. How to Make a Rough Superhydrophobic Surface

With the increasing attention and exploration of the superhydrophobic organisms in nature, scientists figure out that the key to making a rough superhy- drophobic is to create suitable surface microstructures. Nowadays, there have been many ways adopted to manufacturing superhydrophobic surfaces, such as lithography, stretching and etching.

In general, to create a synthetic superhydrophobic surface, two main requirements should be accomplished. That is, the surface should be rough and hydrophobic (low surface energy). These two requirements bring two main methods to produce the superhydrophobic surface:

First and foremost, roughening the surface at the very early stage. It should be emphasized that this method plays a more important role in manufacturing the superhydrophobic surface than the second method.

Secondly, decreasing the surface energy by modifying the component of the surface or applying some chemical materials to the surface.

All the specific technique that mention above like lithography are used to meet these two demands. However, none of these are perfect and they all have its pros and cons.

4.1 Roughening to Create One-Level Structures

4.1.1 Lithography

Lithography is a method to improve the roughness of the surface by etching on the substrate and divided into optical lithography (photolithography), soft lithography, nanoimprint lithography,

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electron beam lithography, X-ray lithog- raphy, and colloidal lithography[37] . It is easy to operate and can be used in a large area of microstructure.

Conventional method of lithography always has a master surface which has the characteristic of superhydrophobic, then using light to transfer the entire information of the geometric pattern from the optical mask to a thin film of photoresist sensitive to light.

With the development of technical means, lithography technology can be accurate to the nanometer level, for example, nanoimprint technology. Lee et al.[22] used this technology to obtain a superhydrophobic surface through a series of experiments.

4.1.2 Chemical or electrochemical techniques

The most widely-used chemical method is etching. Etching techniques are typically used interchangeably with plasma processing or photolithography to produce superhydrophobic surfaces. The progress of this way will be exhibited in Figure 12.

Long et al. [24] used picosecond laser to form periodic nanostructures on the surface of copper matrix, and obtained superhydrophobic materials with a contact angle of about 153°.Khorasani et al.[19] Etching a porous super-hydrophobic material using a carbon dioxide laser on PDMS in 2004.

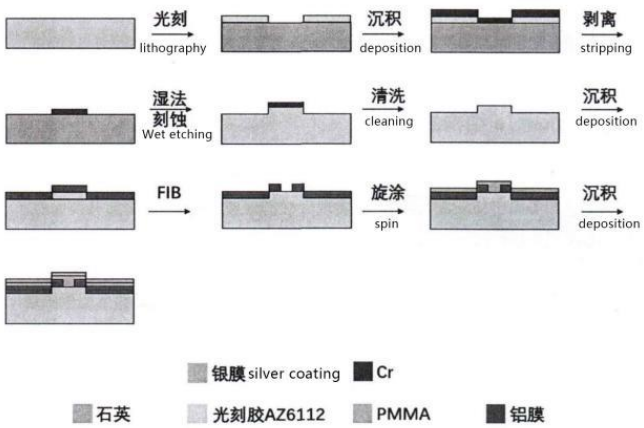

Figure 12. The progress of etching [14]

4.1.3 Stretching

Lee et al. [23] Studied the transition from Wenzel to Cassie state at low strains and found that reversible regulation can be achieved through the shrink- age and recovery of the surface pleated structure (Figure 13). Ren Meng [25] realized the transition from Wenzel to Cassie impregnating wetting state on the superhydrophobic nanocomposite coating with disordered pattern by tensioning and inducing crack to form multi-layered structure.

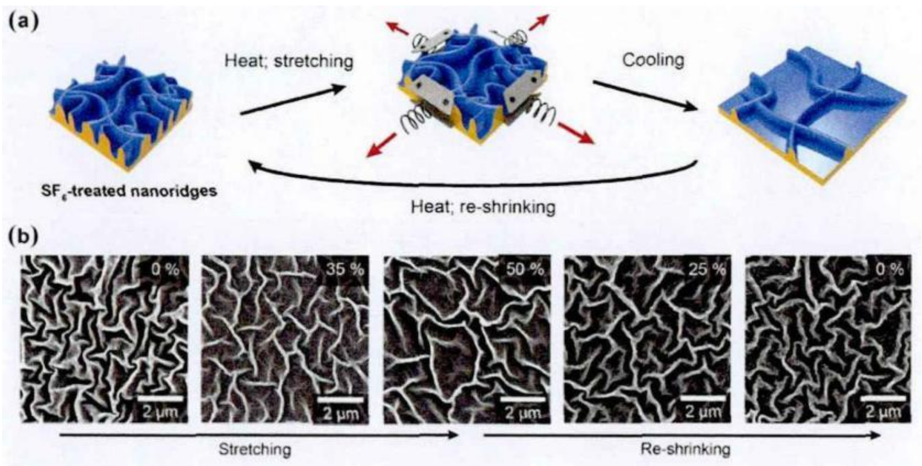

Figure 13. (a) **Controlling** wrinkles by tensile strain. (b) The SEM figure of wrinkles in different tension. [44]

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4.1.4 Deposition

There are many ways to realize deposition such as adsorption, dip coating, electrospinning, anodization, electrochemical, evaporation, chemical vapor de- position (CVD), and plasma [5]. Through electrochemical deposition, rich and compact microstructure will be built on the micro convex surface in a short time, which can effectively roughen the surface and turn it into a superhydrophobic surface. Gu Qinming [29] prepares cross-scale superhydrophobic metal surfaces without low surface energy material modification by picosecond laser-electrochemical deposition (Figure 14).

Liu Yang [2] et al.. made the micro- and nano-sized particles uniformly distributed on the metal surface through the natural deposition of the metal particle suspension, after melting, recrystallization transformation in order to combine with this metal surface, and then modified with low surface energy polymers to prepare superhydrophobic microstructures surface. By this method, a super-hydrophobic microstructural surface was prepared on a brass, 45 steel, 6063 aluminum alloy substrate using tin-lead alloy, and it was found that there is no necessary relationship between the hydrophobic properties of the metal substrate material and the microstructural surface.

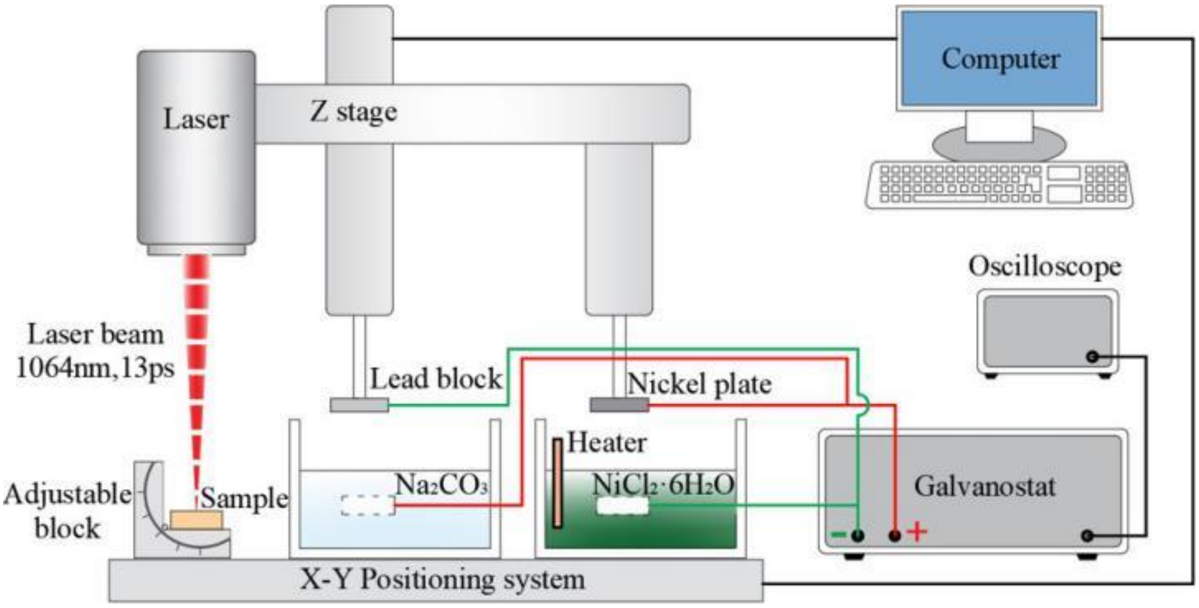

Figure 14. Schematic diagram of experimental system device for picosecond laser cauterization, electrochemical polishing, and electrochemical deposition [29]

4.2 Coating to Create One-Level Hydrophobic Structures

The second category of methods for making superhydrophobic surfaces is to modify the surface with a hydrophobic coating, thereby reducing the surface energy of the surface. Several methods like sol-gel, dip coating, self-assembly, Chemical or physical vapor deposition will be introduced in this section.

4.2.1 Sol-Gel

The sol-gel method uses a compound with a high active ingredient as a precur- sor, and undergoes chemical reactions such as hydrolysis and combination under uniform stirring to form a stable transparent sol system in the solution. The colloid particles in the solution slowly polymerize to form a gel. Sintered and solidified to prepare films or powder materials. And the preparation conditions are mild [21]. Ji Qiang [28] used DTMS (Dodecyltrimethoxysiloxane) to modify alumina nanoparticles to prepare hydrophobic alumina and DTMS composite particles, which were then combined with cotton fabric fibers to successfully prepare a super-hydrophobic cotton fabric coating (Figure 15).

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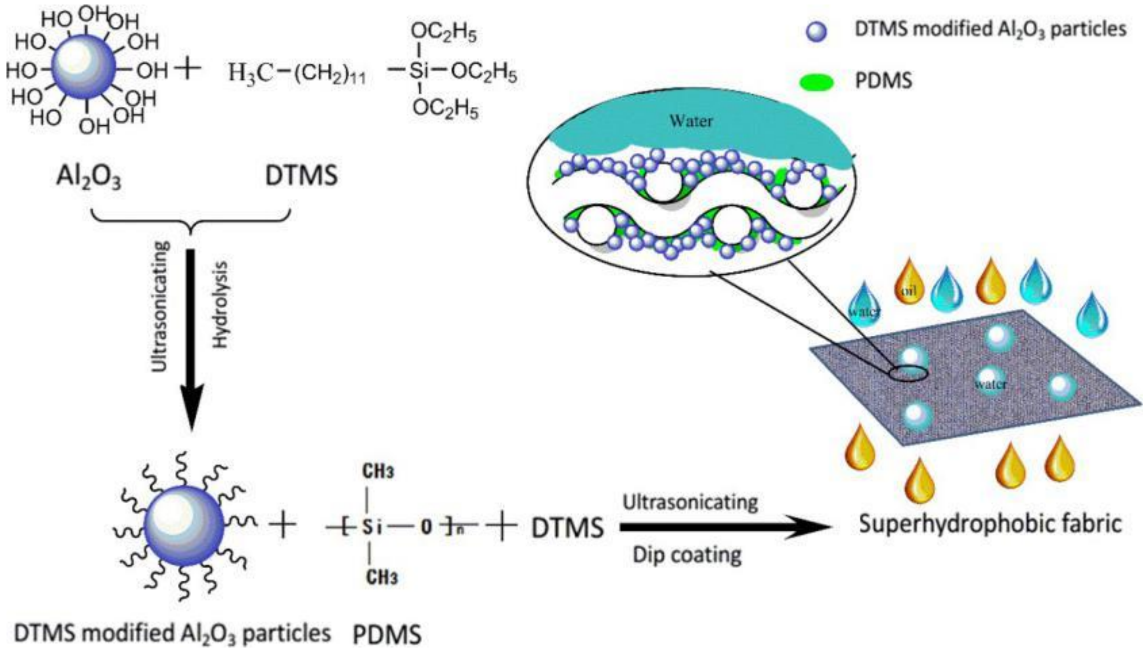

Figure 15. Illustration of the fabrication of superhydrophobic fabrics coatings [28]

4.2.2 Dip Coating

A commonly used coating method is a micro-nanoparticle coating method. This is to mix one or more Micron-sized nanoparticles with a polymer and then apply them to a solid surface by spin coating, spray coating, etc., thereby constructing a hydrophobic structure [31].Chen [6] et al.. Prepared a flame- retardant and self-healing superhydrophobic coating on cotton fabrics by a con- venient solution impregnation method. The coating consists of double layers of APP / bPEi(Branched polyethyleneimine). Zhang [40] et al. mixed micro-nano flower-like ZnO with epoxy resin and formed a superhydrophobic coating on the surface by dip coating (Figure16).

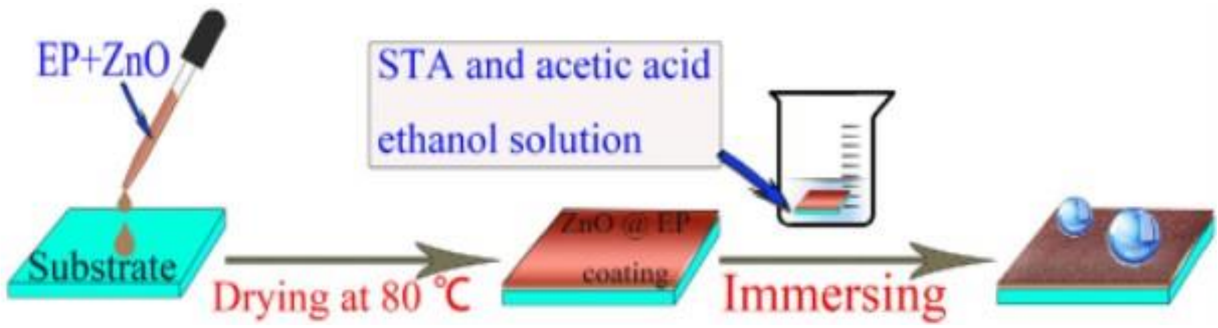

Figure 16. Production process of micro-nanometer surface [40]

4.2.3 Self-Assembly

The layer by layer self-assembly technology is a technology that uses the principle of layer by layer alternate deposition to spontaneously form a multilayer composite structure with complete structure, stable performance and certain specific function on the surface of the substrate through the interaction be- tween anion and anion with opposite charge (such as chemical bond) [8]. At present, many researches have been done on the preparation of super hydrophobic surface by using nanomaterial and polyelectrolyte self-assembly technology. The progress of creating multilayer film will be shown in Figure 17. Lu Qian

[27] obtained super-hydrophobic functional wood by changing the self-assembly maturity and the pH value of the reactants.

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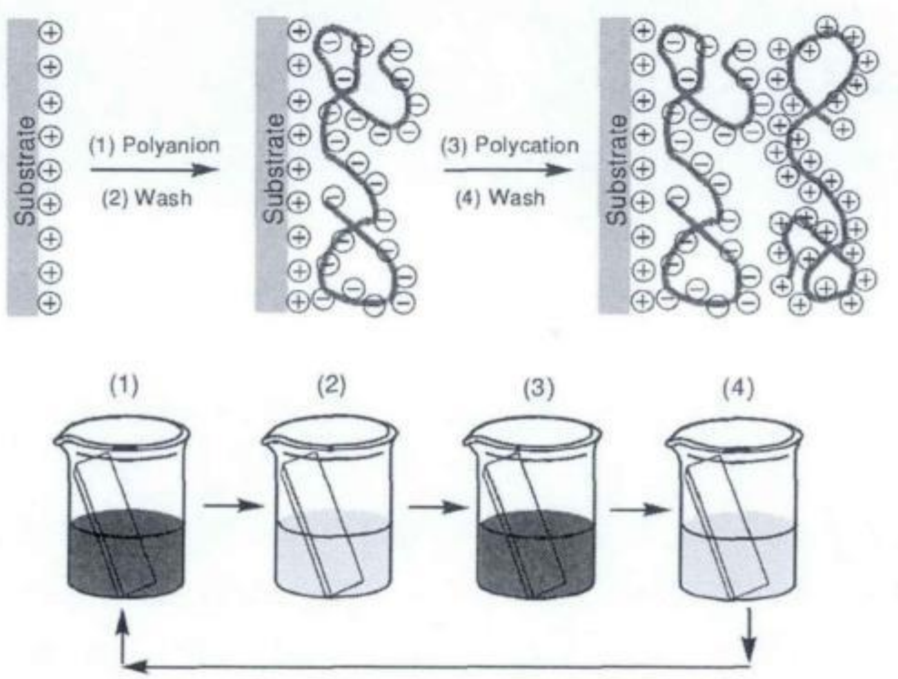

Figure 17. Preparation process of multilayer film [27]

4.2.4 Chemical or Physical Vapor Deposition

In recent decades, with the continuous development of science, electrodepo- sition technology is active in electronic and electrical, mechanical manufactur- ing and many other industries, and electrodeposition technology has gradually becoming a more mature process. This technology is a process of chemical reaction of metal ions (or complex ions) in the electrolyte, reduction on the cathode surface and deposition to obtain metal or alloy. Zhu Yixing [38] intro- duced dopamine into electrodeposition, and prepared functional superhydropho- bic coatings on three different substrate surfaces (steel plate, aluminum plate and copper plate) (Figure 18). Liu Kangkai [18] et al.. used mesoporous sil- ica sol containing Fe precursor as an intermediate and acetylene as a carbon source and carbon nanofibers (CNFs) were uniformly grown on the surface of graphene oxide (GO) films by chemical vapor deposition (CVD). This surface was doped with a layer of fluoropolymer, and finally superhydrophobic graphene nanoparticles (G-CNFs) were obtained.

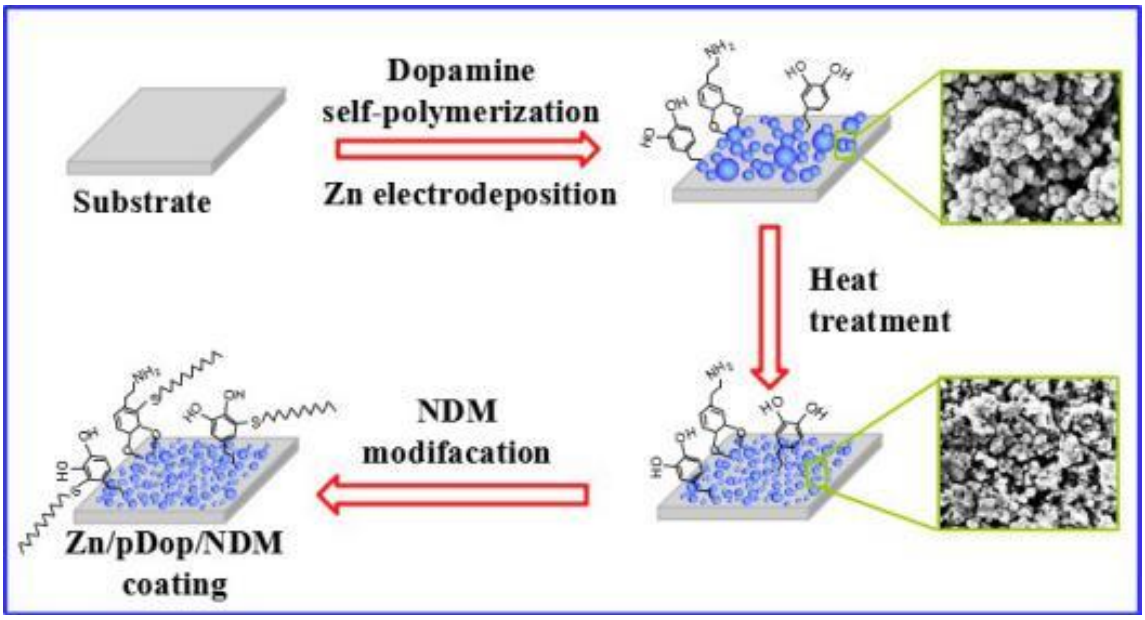

Figure 18. The progress of creating Composite Coating [38]

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4.3 Methods to Create Two-Level (Hierarchical) Struc tures

In nature, many superhydrophobic surfaces two-level structures. The design of the micro-nano two-level structure is derived from the observation of the lotus leaf surface. The reason for us to study this structure is that some results of the few existing condensation experiments on superhydrophobic surfaces show that condensate droplets formed on surfaces with only micron rough structures often lose superhydrophobicity.

When there is only a micro- or nanoscale superhydrophobic surface, the condensate droplets show a wet Wenzel state. As the condensation proceeds, the condensate droplets continue to merge, and the surface will lose superhy- drophobic property. However, for the super hydrophobic surface with two-level structure, the condensate droplets are still in the Cassie Baxter state, and have a small rolling angle, which is easy to separate from the surface[34].

Wen Zhi [41]. adopted a two-step etching method, using hydrofluoric acid to etch the oxide layer on the aluminum surface, and hydrochloric acid to further etch the aluminum substrate to form a micro-nano secondary structure on the aluminum surface Dong He[12] used a wire cutting process to process micron V-shaped and pyramid structures with different depths on the surface of cop- per T2, and then used chemical etching to prepare copper sheets containing V-groove microstructures, pyramid microstructures, and square pyramid microstructures The nanostructure finally formed the surface of the micro-nano secondary structure(Figure 19).

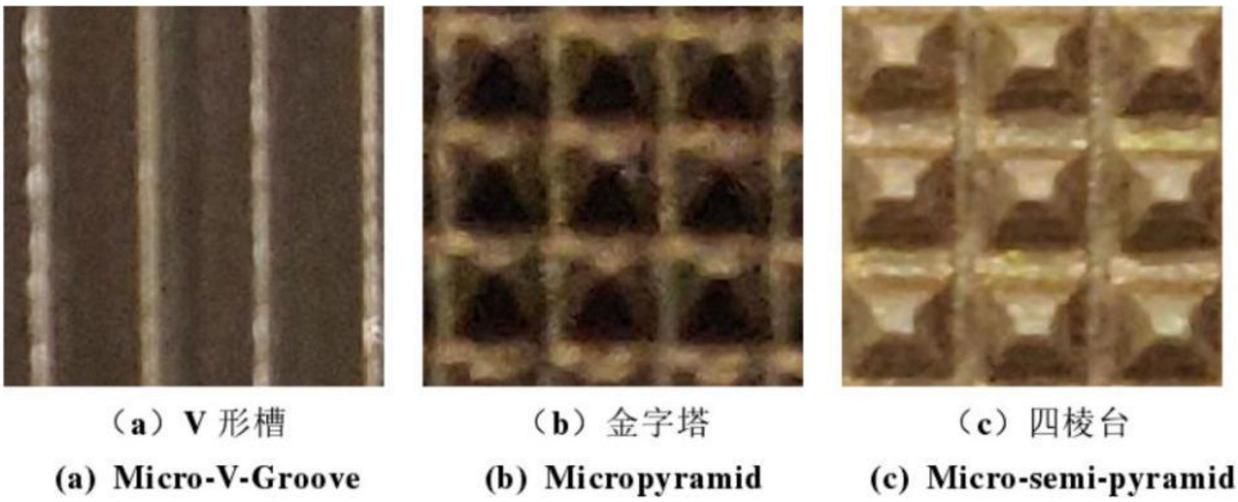

Figure 19. Microstructures shown schematically [12]

4.4 Limitations of Current Technologies

The size of the pattern formed by photolithography is limited by the inher- ent characteristics of light diffraction, the high-energy radiation equipment of forming minute patterns has a complicated structure as well as high technical requirements, and is difficult to apply to uneven surfaces. Besides, the pho- tolithography process is complex and the equipment expensive [15].

Electrical etching technology is a direct and effective method for preparing rough surfaces. Rough surfaces with different structures can be prepared by changing the etching time and radio frequency power. However, the mechanical strength of the rough surface is low, making the stability of superhydrophobic very poor, and its effect gradually weakens as the storage time increases. At the same time, this method has expensive equipment, high cost, and chemical pollution [16].

The stretching method is simple, the cost is low, and a superhydrophobic surface with a large area can be obtained. But the current research is not enough and more research in this field is needed.

The deposition and melting method mentioned in the article can achieve the preparation of micron-level topography, and it has the advantages of high processing efficiency, simple process, low cost,

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and does not affect the strength of the original workpiece, but the problem that it is difficult to apply to the curved surface needs further study [2].

The sol-gel method has certain advantages for the preparation of inorganic superhydrophobic materials such as ZnO, TiO2, and Al2O3, but it has the disadvantages of longer process routes, solvent contamination, and higher costs [36].

Simple brushing, dipping and spraying methods can well overcome the dis- advantages of complex and time-consuming, expensive equipment and limited types of substrate materials, but the micro-nano structure on the surface produced is easily damaged and lost superhydrophobic characteristic [1]. For the layer-by-layer self-assembly method, the poor stability of the coating driven by weak bonds such as hydrogen bonding or electrostatic interaction and the large number of assembly layers limit its application in superhydrophobic coatings. Besides it also required a suitable precursor, making it more complicated [8].

The chemical vapor deposition method can obtain surfaces with different hydrophobic properties by changing the chemical deposition atmosphere. This method has certain research value, but it is currently expensive to prepare and is not conducive to large-scale. production [16].

5. Evaluation of Surface Durability

Superhydrophobic surface refers to the surface where the contact angle of liquid drops on the solid surface is greater than 150° and the rolling angle is less than 10°. This kind of surface has many unique characteristics, such as self- cleaning ability, anti-icing ability, super hydrophobicity and so on [39]. As we all know, the micro rough structure of the papilla on the surface of lotus leaf is one of the important reasons for its super hydrophobicity. But at the same time, this kind of micro nanostructure has poor adaptability to the environment. Some chemical or physical mechanical wear, such as various organic solvent reagents, dust, particles, ultraviolet irradiation, etc., will lead to the change of its surface structure, resulting in the loss of its surface hydrophobicity. Therefore, many methods are used to improve the durability of superhydrophobic surface, so as to extend its service life, increase its application value and expand its application field.

5.1 Reasons for Poor Durability of Superhydrophobic Surface

5.1.1 Chemical Properties

The properties of all substances are related to the stability of their own chemical properties. Similarly, the durability of superhydrophobic surface is closely related to its chemical stability. In the face of all kinds of complex environ- ment, some organic solvents such as acid, alkali, salt, ultraviolet radiation, dust and so on will make the chemical properties of superhydrophobic surface change unevenly, thus making the surface lose the superhydrophobic performance.

5.1.2 Mechanical Abrasion

Mechanical wear also affects the superhydrophobic properties of superhy- drophobic surfaces [26]. As we all know, the contact angle of superhydrophobic surface is larger and its surface energy is lower. Mechanical wear causes the con- sumption of low surface energy materials on superhydrophobic surfaces, while the increase of surface energy will lead to poor hydrophobicity.

5.2 Test Method for Durability of Superhydrophobic Sur- faces

Due to the poor durability of superhydrophobic surface, there are many re- searchers to improve the superhydrophobic surface, and therefore there are many test methods to evaluate the surface durability. For example, tangential wear method, waterfall / jet test, AFM and ball-on-flat tribometer tests, etc.

5.2.1 Tangential Wear Method

Tangential wear method is a common method used to test the durability of superhydrophobic surface. The specific method is to use abrasive paper, textiles, rubber and other items as abrasive materials to carry out mechanical wear on the superhydrophobic surface. By changing the pressure, contact area,

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movement mode, movement speed and track, the control variable method is adopted to detect the durability of superhydrophobic surface.

5.2.2 Waterfall / Jet Test

Waterfall / jet test is also a method to measure the durability of superhy- drophobic surface exposed to water for a long time. The durability of the surface can be judged by changing the surface water pressure and observing the rela- tionship between the static contact angle and the contact angle delay exposure time.

Jung and Bhushan [5] conducted waterfall / jet test on the surface made of CNT and lotus wax. In the first experiment, the synthesized surface was ex- posed to water pressure of 10 kPa for 24 hours. With the increase of time, the phenomenon observed was that the static contact angle decreased slightly but remained above 150 ° and the contact angle lag increased slightly but remained below 15 °. In a second experiment, the synthesized surface was exposed to a pressure of 0 to 45 kPa for 20 minutes. With the increase of water pressure, the phenomenon observed is that the static contact angle decreases and the contact angle lag slightly increases, but its structure and hydrophobicity have not changed significantly. According to the experimental results, the superhy- drophobic material can still show good wettability and durability when exposed to water for a long time or under high pressure.

5.2.3 AFM and Ball-On-Flat Tribometer Tests

In order to further study the durability of CNT materials prepared by Jung and Bhushan [5], they carried out a cyclic wear test using AFM under two normal loads of 100 NN and 10 LN, and using wear marks made by borosilicate balls. Under two different loads, the degree of wear marks on the surface is not the same. Under the normal load of 100 NN, the wear marks are not obvious. Under the normal load of 10ln, the depth of the wear scar did not change much, but the surface morphology was slightly different from that before the wear test. The experiment shows that the structure should be changed under high normal load. At the same time, the same experiment was carried out on the nano structure prepared by Lotus wax, and the similar results were obtained.

At the same time, in order to study the durability of the CNT surface under high load, Jung and Bhushan [5] carried out the conventional plane ball-on-flat tribometer tests on the CNT surface. In this experiment, the friction coefficients of nano structure and layered structure of CNT materials were measured respectively, and the relationship between them and the number of cycles was found out. It is found that the friction coefficient of the two structures has little change in the whole experimental process, and the optical microscope image is obtained before and after the wear test. Comparing the front and rear surfaces, it is found that there is no wear or the wear is very small. This shows that CNT surface has better durability. After the research of CNT material, the same experiment was carried out on the surface prepared by Lotus wax, and the similar result was obtained, which also has better durability. Comparing the two materials, it can be found that the mechanical durability of super hydrophobic CNT composite structure is better than that of the surface with lotus wax structure, and it can be widely used in practical life.

6. Closure

Nowadays superhydrophobic surface plays an improtant role many other areas. It is widely used in industry and have a great protential in the future manufacturing. But up to now, it is still a big challenge to prepare superhydrophobic surface with better performance and improve the durability of superhydrophobic surface.

6.1 Conclusion

In this paper, expect the classical model of hydrophobicity theory like surface tension, surface energy, and contact angle , factors that lead to the superhydrophobic properties of solid surfaces are also analyzed. Surface energy and surface roughness are the main factors. In addition, this report also mentioned that the hierarchical structure can also affect the surface hydrophobicity.

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Afterwards, we discussed how these theories are applied to several natural superhydrophobic surfaces in plants and insects, including lotus leaves, rose petals, butterfly wings and rice leaves. By identifying the common characteristics of each of these surfaces, we analyzed how different structural and compositional characteristics determine their different wetting properties.

We also illustrate many advanced and testing methods such as lithography, deposition, stretching, sol-gel, etc. to create one-level and two-level synthetic superhydrophobic surface, and also show the pros and cons of these methods.

Lastly, several methods such as washing test method, tape stripping test method, impact method, are introduced in this paper. When choosing testing methods, we should combine the characteristics of the materials to make appropriate selection.

6.2 Limitation

However, some classic superhydrophobic states are not mentioned in the article, such as the transition state between Wenzel state and Cassie state and the gecko state.

Besides, due to space limitations, we have not introduced all methods of making superhydrophobic surfaces, such as electrostatic spinning, hydrothermal synthesis etc., instead, we only illustrate some more general and important ways like lithography, deposition and so on, which have been generally applicable in production.

In terms of the test methods, so far there is no unified and standardized method to measure the durability of superhydrophobic materials. It is suggested that in this respect, specific mechanical durability standards can be formulated for different testing types.

Finally, since we focus our attention on illustrate the nature and synthetic hydrophobic surfaces, in this essay, we do not talk about the application of the synthetic superhydrophobic surface like anti-icing, anti-contamination and many other fields.

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